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# Metallo-Ligand [Cu$^{II}$(carboxylato)$_4$]$^{2+}$ Cores: Tetrakis(trimethylammonioacetato-*O*)copper Diperchlorate and its 1/1 Complex with Sodium Perchlorate

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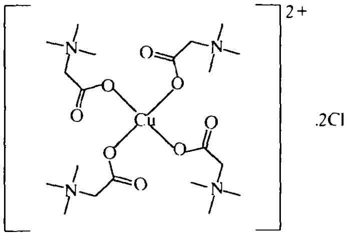
## Abstract

The crystal structure of tetrakis(trimethylammonioacetato-*O*)copper diperchlorate, $[Cu(C_5H_{11}NO_2)_4](ClO_4)_2$, consists of discrete $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ cations and $ClO_4^-$ anions. The Cu atom is coordinated by four trimethylammonioacetate ligands in a square-planar geometry. The compound forms a 1/1 complex with sodium perchlorate, *i.e.* perchlorato-2$\kappa O$-bis($\mu$-trimethylammonioacetato)-1:2$\kappa^4 O$-bis(trimethylammonioacetato)-1$\kappa^2 O$-coppersodium diperchlorate, $[Cu(C_5H_{11}NO_2)_4\{Na(ClO_4)\}](ClO_4)_2$, in which the Cu and Na atoms are bridged by either three $\mu_2$-carboxylato-*O*,*O*′ or two $\mu_2$-carboxylato-*O* groups to give rise to a linear cationic chain.

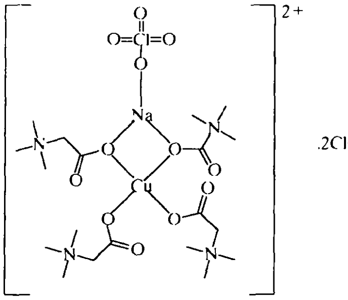
## Comment

Four zwitterionic betaine molecules (or other betaine homologs) can be assembled around a Cu$^{II}$ atom to provide a [Cu(betaine)$_4$]$^{2+}$ 'metallo-ligand' core that binds to hard metal ions such as Li$^{I}$, Ca$^{II}$ and La$^{III}$ ions through the carboxyl oxygen ends (Chen & Mak, 1994*a*,*b*; Wu *et al.*, 1995). The charges of the cation are typically balanced by perchlorate anions, such anions being chosen because of their lack of Lewis basicity, and several octadecanuclear copper–lanthanoid clusters have been synthesized. Interestingly, their crystal structures reveal the presence of an encapsulated perchlorate ion (Chen *et al.*, 1995, 1996). The tetrakis(trimethylammonioacetato-*O*)copper perchlorate homolog itself has not been crystallographically examined, although the metallo-ligand core has been authenticated in the nitrate (Chen & Mak, 1991).

The crystal structure of tetrakis(trimethylammonioacetato-*O*)copper diperchlorate, (I), consists of discrete $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ cations and $ClO_4^-$ anions.



(I)



(II)

The Cu atom occupies the Wyckoff position 2*a* (point symmetry: $\bar{4}2m$ or *D2d*) and is coordinated by four trimethylammonioacetate ligands. The Cu atom shows almost idealized square-planar coordination [Cu—O = 1.948 (2) Å; O—Cu—O$_{cis}$ = 90.0 (1) and O—Cu—O$_{trans}$ = 177.5 (3)°]. The four double-bonded O atoms point into the square plane [Cu···O = 2.906 (4) Å], so that the ligands complex to the metal atom in an up/down–up/down–up/down–up/down fashion, if the Cu···O interaction is regarded as a weak bond (Fig. 1). The coordination environment of the Cu atom in (I) is similar to that of the Cu atom in tetrakis(trimethylammonioacetato-*O*)copper nitrate [Cu—O = 1.948 (3) and Cu···O = 2.833 (3) Å; Chen & Mak, 1991]. The ligating behavior of the trimethylammonioacetate ligand in both complexes differs from that of the pyridiniopropionate ligand; in the latter complex, the pyridiniopropionate molecules ligate the Cu atom in a centrosymmetric up/down manner (Chen & Mak, 1992).

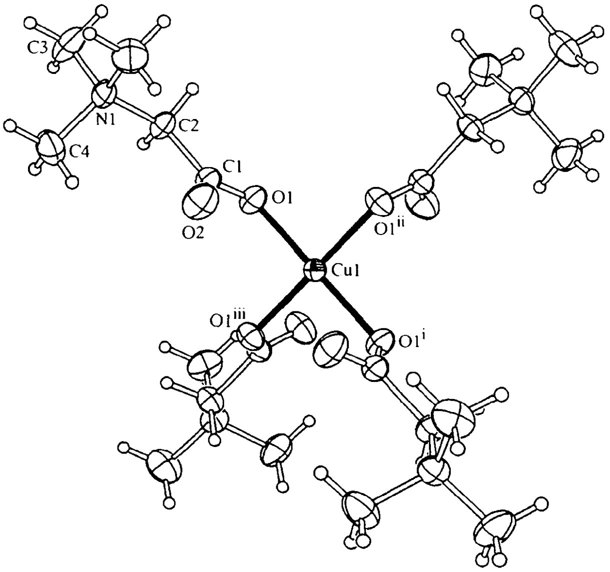


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I), with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The disordered perchlorate ion is not shown. [Symmetry codes: (i) $2-x, 2-y, z$; (ii) $2-y, x, -z$; (iii) $y, 2-x, -z$.]

The $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ metallo-ligand core has been used to bind to Li and Ca atoms; the Li atom shows tetrahedral coordination, whereas the Ca atom shows dodecahedral coordination (Chen & Mak, 1994*b*). The 1/1 complex of tetrakis(trimethylammonioacetate)copper diperchlorate with sodium perchlorate, (II), which was obtained when an excess of sodium perchlorate was used in the reaction, confirms the coordinating ability of the $[Cu\{(CH_3)_3NCH_2CO_2\}_4]^{2+}$ core towards Na. The Cu atom occupies the Wyckoff position 2*a*, of symmetry *m*, and is covalently bonded to four carboxyl O atoms [Cu—O = 1.94 (2)–1.96 (2) Å] in an approximately square-planar geometry [$O—Cu—O_{trans}$ = 170.5 (6) and 172.2 (5)°] (Fig. 2). The betaine ligands complex to the metal atom in a three-up/one-down fashion, this mode being previously documented in the copper–calcium complex (Chen & Mak, 1994*a*). The Na atom is surrounded by an irregular octahedron of six O atoms, one of which belongs to the perchlorate group [Na—O = 2.31 (1)–2.489 (6) Å]. The electrostatic Na—O interactions are similar to those found in sodium perchlorate monohydrate, whose Na atom also shows irregular octahedral coordination [average Na—O = 2.390 Å; Berglund *et al.*, 1975]. The three-up/one-down arrangement of the betaine ligands may be attributed to perturbation by Na atoms, resulting in a 'carboxy-

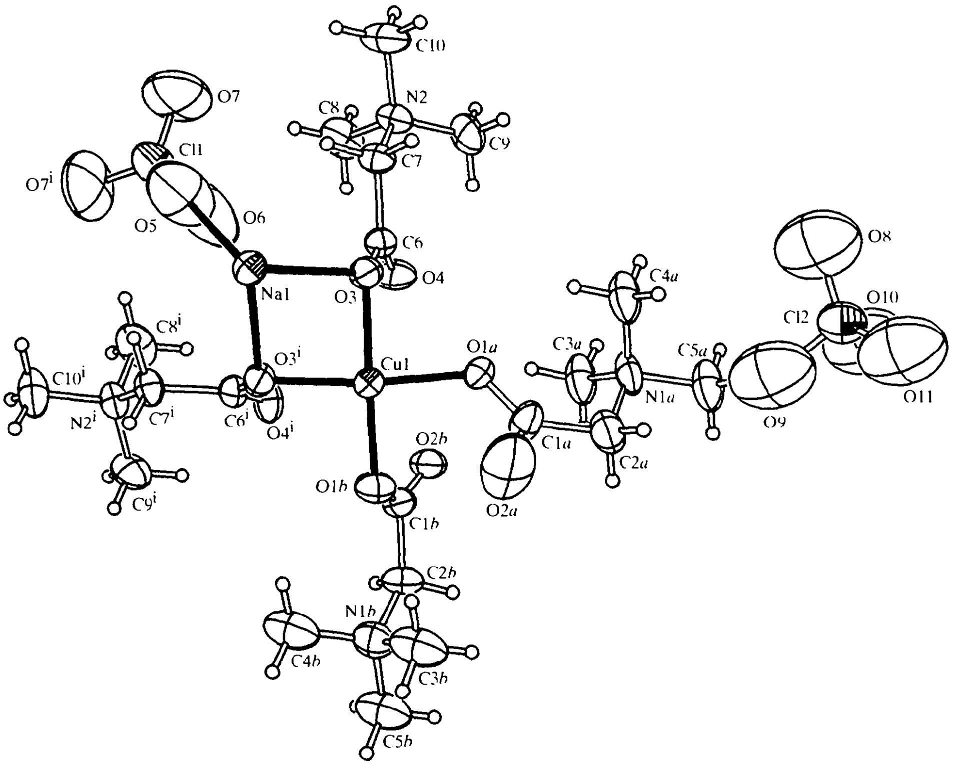


Fig. 2. *ORTEP*II (Johnson, 1976) plot of (II), with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. Disorder in the free perchlorate ion is not shown. [Symmetry code: (i) $x, -y, z$.]

late-shift' phenomenon (Chen & Mak, 1994*a*,*b*; Watton *et al.*, 1995). The isolation of the present complex gives additional confirmation of the observation that a coordinated carboxylate group can shift around a metal atom under the perturbing influence of another metal ion. The double-bonded carboxyl O atoms interact only weakly with the Cu atom [Cu—O = 2.911 (6)–3.26 (2) Å]. Each pair of adjacent Cu and Na atoms is bridged by either three $\mu_2$-carboxylato-*O*,*O'* or two $\mu_2$-carboxylato-*O* groups to furnish a one-dimensional cationic chain running along the *c* axis.

## Experimental

For the preparation of (I), trimethylammonioacetate (betaine; 0.55 g, 4.0 mmol) and $Cu(NO_3)_2.6H_2O$ (0.24 g, 1.0 mmol) were dissolved in water (8 ml) and warmed briefly. The addition of an aqueous solution (2 ml) of $NaClO_4.H_2O$ (0.14 g, 2.0 mmol) resulted in a deep-blue solution. After several days, blue–lilac polyhedral crystals were deposited and the compound was isolated in about 70% yield (found: C 32.93, H 6.15, N 7.80%; calculated for $C_{20}H_{44}Cl_2CuN_4O_{16}$: C 32.86, H 6.07, N 7.66%). IR data: 3472 (*w*, *br*), 3057 (*m*), 3036 (*m*), 2987 (*m*), 1651 (*vs*), 1492 (*m*), 1475 (*s*), 1390 (*vs*), 1232 (*w*), 1096 (*vs*), 990 (*m*), 962 (*w*), 927 (*s*), 906 (*s*), 776 (*w*), 723 (*m*), 615 (*w*), 582 (*m*), 456 (*m*) cm$^{-1}$. For the preparation of (II), betaine (0.55 g, 4.0 mmol) and $Cu(NO_3)_2.6H_2O$ (0.24 g, 1.0 mmol) were dissolved in water (8 ml). An aqueous solution (4 ml) of $NaClO_4.H_2O$ (0.32 g, 4.5 mmol) was added slowly to give a deep-blue solution; blue plate-like crystals were obtained in about 30% yield after about a week (found: C 28.30, H 5.12, N 6.47%; calculated for $C_{20}H_{44}Cl_3CuN_4NaO_{20}$: C 28.15, H 5.20, N 6.56%). IR data: 3472 (*m*, *br*), 3064 (*w*), 3008 (*w*), 2966 (*w*), 1665 (*vs*), 1630 (*s*), 1482 (*s*), 1398 (*vs*), 1328 (*s*), 1236 (*w*), 1096 (*vs*), 983 (*w*), 962 (*w*), 927 (*m*), 906 (*s*), 779 (*w*), 723 (*m*), 625 (*s*), 575 (*w*), 463 (*w*) cm$^{-1}$.

### Compound (I)

*Crystal data*

$[Cu(C_5H_{11}NO_2)_4](ClO_4)_2$
$M_r = 731.03$
Tetragonal
$I\bar{4}2m$
$a = 11.711\ (1)$ Å
$c = 11.696\ (1)$ Å
$V = 1604.1\ (3)$ Å$^3$
$Z = 2$
$D_x = 1.513$ Mg m$^{-3}$
$D_m$ not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.0$–$13.0°$
$\mu = 0.922$ mm$^{-1}$
$T = 298\ (2)$ K
Block
0.5 × 0.5 × 0.5 mm
Blue–lilac

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$ scan
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.566$, $T_{max} = 0.631$
1339 measured reflections
712 independent reflections

695 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 29.94°$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 16$
3 standard reflections every 60 reflections intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 0.936$
712 reflections
76 parameters
H atoms: riding model, $U(H) = 1.5U_{eq}(C)$
$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 2.9286P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.391$ e Å$^{-3}$
$\Delta\rho_{min} = -0.420$ e Å$^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.032 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack & Schwarzenbach (1988)
Flack parameter = 0.05 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (*I*)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 1 | 1 | 0 | 0.0202 (2) |
| Cl1† | 0.9815 (3) | 0.5110 (9) | 0.006 (1) | 0.035 (2) |
| O1 | 0.8824 (1) | 0.8824 (1) | −0.0036 (4) | 0.0319 (5) |
| O2 | 0.8848 (2) | 0.8848 (2) | 0.1874 (3) | 0.0436 (9) |
| O3† | 1.012 (1) | 0.482 (1) | 0.121 (1) | 0.072 (2) |
| O4† | 1.007 (2) | 0.629 (1) | −0.018 (2) | 0.072 (2) |
| O5† | 0.860 (1) | 0.501 (2) | −0.010 (2) | 0.072 (2) |
| O6† | 1.036 (1) | 0.436 (1) | −0.074 (1) | 0.072 (2) |
| N1 | 0.7090 (2) | 0.7090 (2) | 0.1929 (3) | 0.0306 (7) |
| C1 | 0.8495 (2) | 0.8495 (2) | 0.0948 (4) | 0.0271 (7) |
| C2 | 0.7579 (2) | 0.7579 (2) | 0.0846 (3) | 0.0285 (7) |
| C3 | 0.6223 (3) | 0.6223 (3) | 0.1600 (6) | 0.052 (1) |
| C4 | 0.7993 (3) | 0.6513 (4) | 0.2629 (3) | 0.0461 (9) |

† Site occupancy = 0.25.

Table 2. *Selected geometric parameters* (Å, °) *for* (*I*)

| | | | |
|---|---|---|---|
| Cu1—O1 | 1.948 (2) | Cu1—O1$^{ii}$ | 1.948 (2) |
| Cu1—O1$^{i}$ | 1.948 (2) | Cu1—O1$^{iii}$ | 1.948 (2) |
| O1—Cu1—O1$^{i}$ | 177.5 (3) | O1$^{i}$—Cu1—O1$^{iii}$ | 90.0 (1) |
| O1—Cu1—O1$^{iii}$ | 90.0 (1) | O1$^{i}$—Cu1—O1$^{ii}$ | 90.0 (1) |
| O1—Cu1—O1$^{ii}$ | 90.0 (1) | O1$^{iii}$—Cu1—O1$^{ii}$ | 177.5 (3) |

Symmetry codes: (i) $2 - x, 2 - y, z$; (ii) $2 - y, x, -z$; (iii) $y, 2 - x, -z$.

### Compound (II)

*Crystal data*

$[CuNa(C_5H_{11}NO_2)_4(ClO_4)]$-$(ClO_4)_2$
$M_r = 853.47$
Monoclinic
*Cm*
$a = 12.6528\ (8)$ Å
$b = 25.849\ (1)$ Å
$c = 5.7717\ (4)$ Å
$\beta = 102.626\ (4)°$
$V = 1842.1\ (2)$ Å$^3$
$Z = 2$
$D_x = 1.539$ Mg m$^{-3}$
$D_m$ not measured

Mo *Kα* radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.25$–$12.75°$
$\mu = 0.903$ mm$^{-1}$
$T = 298\ (2)$ K
Plate
0.44 × 0.36 × 0.12 mm
Blue

*Data collection*

Enraf–Nonius CAD-4 diffractometer

2501 reflections with $I > 2\sigma(I)$

$\omega$ scan
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{min} = 0.635$, $T_{max} = 0.897$
2845 measured reflections
2845 independent reflections
$\theta_{max} = 29.97°$
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 36$
$l = -8 \rightarrow 7$
3 standard reflections
frequency: 60 min
intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.075$
$wR(F^2) = 0.195$
$S = 1.466$
2845 reflections
278 parameters
H atoms: riding model, $U(H) = 1.5U_{eq}(C)$
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.086$ e Å$^{-3}$
$\Delta\rho_{min} = -0.909$ e Å$^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.005 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack & Schwarzenbach (1988)
Flack parameter = 0.14 (3)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.00425 (8) | 0 | −0.0021 (1) | 0.0315 (3) |
| Cl1 | −0.4204 (3) | 0 | 0.1119 (6) | 0.0617 (8) |
| Cl2† | 0.4525 (2) | 0.2488 (1) | 0.2326 (3) | 0.0561 (5) |
| Cl2*a*‡ | 0.4525 (2) | 0.2488 (1) | 0.2326 (3) | 0.0561 (5) |
| Na1 | −0.1371 (3) | 0 | 0.4030 (6) | 0.0334 (7) |
| O5 | −0.3229 (9) | 0 | 0.268 (4) | 0.18 (1) |
| O6 | −0.386 (2) | 0 | −0.113 (3) | 0.23 (2) |
| O7 | −0.4753 (8) | 0.0444 (3) | 0.101 (3) | 0.137 (5) |
| O8† | 0.3701 (2) | 0.2755 (8) | 0.288 (4) | 0.162 (5) |
| O9† | 0.441 (2) | 0.1942 (7) | 0.268 (4) | 0.162 (5) |
| O10† | 0.449 (2) | 0.2551 (9) | −0.014 (3) | 0.162 (5) |
| O11† | 0.556 (2) | 0.2606 (8) | 0.358 (4) | 0.162 (5) |
| O8*a*‡ | 0.336 (3) | 0.259 (2) | 0.133 (7) | 0.21 (2) |
| O9*a*‡ | 0.521 (4) | 0.283 (2) | 0.129 (7) | 0.21 (2) |
| O10*a*‡ | 0.475 (4) | 0.194 (1) | 0.174 (6) | 0.21 (2) |
| O11*a*‡ | 0.475 (4) | 0.253 (1) | 0.493 (6) | 0.21 (2) |
| O1*a*§ | 0.097 (2) | 0.0584 (9) | −0.045 (3) | 0.040 (4) |
| O2*a*§ | 0.260 (1) | 0.030 (1) | 0.157 (4) | 0.122 (9) |
| N1*a*§ | 0.200 (2) | 0.1341 (6) | −0.283 (3) | 0.043 (5) |
| C1*a*§ | 0.204 (1) | 0.0585 (6) | 0.007 (3) | 0.048 (3) |
| C2*a*§ | 0.268 (1) | 0.0954 (9) | −0.117 (4) | 0.069 (6) |
| C3*a*§ | 0.121 (2) | 0.1065 (8) | −0.477 (4) | 0.077 (6) |
| C4*a*§ | 0.142 (2) | 0.1689 (8) | −0.147 (4) | 0.077 (6) |
| C5*a*§ | 0.274 (2) | 0.1672 (8) | −0.396 (4) | 0.077 (6) |
| O1*b*§ | 0.093 (2) | −0.0489 (9) | −0.129 (4) | 0.052 (5) |
| O2*b*§ | 0.048 (1) | −0.0157 (4) | −0.490 (2) | 0.050 (3) |
| N1*b*§ | 0.219 (1) | −0.1257 (6) | −0.289 (3) | 0.041 (5) |
| C1*b*§ | 0.089 (1) | −0.0477 (5) | −0.347 (2) | 0.037 (2) |
| C2*b*§ | 0.152 (1) | −0.0873 (7) | 0.463 (3) | 0.057 (5) |
| C3*b*§ | 0.306 (2) | −0.0990 (9) | −0.104 (4) | 0.063 (4) |
| C4*b*§ | 0.147 (2) | −0.1607 (8) | −0.177 (5) | 0.063 (4) |
| C5*b*§ | 0.275 (2) | −0.1597 (8) | −0.449 (4) | 0.063 (4) |
| O3 | −0.0950 (4) | 0.0517 (2) | 0.0708 (9) | 0.038 (1) |
| O4 | −0.1531 (5) | 0.0644 (2) | −0.3183 (9) | 0.048 (1) |
| N2 | −0.3011 (5) | 0.1432 (2) | −0.2340 (9) | 0.036 (1) |
| C6 | −0.1532 (5) | 0.0734 (3) | −0.110 (1) | 0.034 (1) |
| C7 | −0.2296 (6) | 0.1133 (3) | −0.040 (1) | 0.036 (1) |
| C8 | −0.3769 (7) | 0.1067 (4) | −0.393 (2) | 0.059 (2) |
| C9 | −0.2389 (8) | 0.1731 (3) | −0.376 (2) | 0.053 (2) |
| C10 | −0.3687 (9) | 0.1782 (4) | −0.119 (2) | 0.062 (2) |

† Site occupancy = 0.67. ‡ Site occupancy = 0.33. § Site occupancy = 0.50.

Table 4. *Selected geometric parameters (Å, °) for (II)*

| | | | |
|---|---|---|---|
| Cu1—O1*a* | 1.96 (2) | Na1—O3 | 2.489 (6) |
| Cu1—O1*b* | 1.94 (2) | Na1—O3$^{i}$ | 2.489 (6) |
| Cu1—O3 | 1.942 (5) | Na1—O4$^{iii}$ | 2.354 (5) |
| Cu1—O3$^{i}$ | 1.942 (5) | Na1—O4$^{ii}$ | 2.354 (5) |
| Na1—O2*b*$^{ii}$ | 2.33 (1) | Na1—O5 | 2.31 (1) |
| O1*a*—Cu1—O1*b* | 92.4 (6) | O3—Na1—O3$^{i}$ | 65.0 (3) |
| O1*a*—Cu1—O3 | 86.1 (6) | O3—Na1—O4$^{iii}$ | 102.2 (2) |
| O1*a*—Cu1—O3$^{i}$ | 172.2 (5) | O3—Na1—O4$^{ii}$ | 166.2 (2) |
| O1*b*—Cu1—O3 | 170.5 (6) | O3—Na1—O5 | 96.5 (5) |
| O1*b*—Cu1—O3$^{i}$ | 95.0 (7) | O3$^{i}$—Na1—O4$^{iii}$ | 166.2 (2) |
| O3—Cu1—O3$^{i}$ | 87.0 (3) | O3$^{i}$—Na1—O4$^{ii}$ | 102.2 (2) |
| O2*b*$^{ii}$—Na1—O3 | 74.8 (3) | O3$^{i}$—Na1—O5 | 96.5 (5) |
| O2*b*$^{ii}$—Na1—O3$^{i}$ | 85.7 (3) | O4$^{iii}$—Na1—O4$^{ii}$ | 90.0 (3) |
| O2*b*$^{ii}$—Na1—O4$^{iii}$ | 85.9 (3) | O4$^{iii}$—Na1—O5 | 89.8 (5) |
| O2*b*$^{ii}$—Na1—O4$^{ii}$ | 100.1 (3) | O4$^{ii}$—Na1—O5 | 89.8 (5) |
| O2*b*$^{ii}$—Na1—O5 | 169.2 (3) | | |

Symmetry codes: (i) $x, -y, z$; (ii) $x, -y, 1 + z$; (iii) $x, y, 1 + z$.

In (I), the perchlorate is disordered over two positions and was refined with occupancies of 0.25 for the O atoms. The group was constrained as a tetrahedron with two *SADI* instructions; an *EADP* restraint in *SHELXL*97 (Sheldrick, 1997*a*) was also used. The disorder was not suspected in the earlier stages of refinement; the Cl atom appeared to be bonded to three O atoms, which were also in special positions. The model refined smoothly as $[Cu(betaine)_4][H_2ClO_6]_2$, but this was ruled out by the C, H and N analytical values. The final difference map for this model had minima and maxima of about ±1 e Å$^{-3}$. The correct model yielded a final difference map that was virtually diffuse, with minima and maxima of only ±0.4 e Å$^{-3}$. The present refinement is an improvement on the previously published structure (McEwen, 1973), which did not include the O atoms of the perchlorate group in the calculations ($R = 0.09$). The Cu—O bond distance is given as 1.89 (1) Å in the earlier report; the intramolecular Cu—$O_{carbonyl}$ interaction is given as 2.09 (2) Å, which must be erroneous. In (II), one of the two betaines (O1, O2, N1, C1–C5) is disordered over two positions and it was refined with two approximately mirror-related ligands, each of 0.5 site occupancy. For both halves, the $C_4N$ unit was refined as a tetrahedron with the appropriate *SADI* instruction in *SHELXL*97. The C—N distances were fixed using *DFIX* at 1.54±0.01 Å and the C1···N1 distances at 2.52±0.02 Å. An *EADP* instruction was used on the three methyl groups. One of the two perchlorate groups is also disordered over two positions, and this was refined as two $ClO_4$ groups, of 0.67 and 0.33 site occupancies, sharing a common Cl atom. A set of *SADI* and *EADP* instructions was used on each. The *PLATON* (Spek, 1990) suite suggested two solvent-accessible voids at (0.427,0,0.545) and (0.927,0,0.545) in the unit cell, but their volumes (19.3 Å$^3$ each) are too small to accommodate water molecules. The final difference map had a peak of about 1 e Å$^{-3}$ at 2 Å from O2*a*, and a hole of about −1 e Å$^{-3}$ at 1 Å from Cu1.

For both compounds, data collection: *CAD*-4/*PC* (Kretschmar, 1994); cell refinement: *CELDIM* (Enraf–Nonius, 1988); data reduction: *XCAD*4 (Harms, 1997); program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*b*); program(s) used to refine structures: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1268). Services for accessing these data are described at the back of the journal.

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# *catena*-Poly[(dichlorodimethyltin)-$\mu$-(4,4′-bipyridine-*N*:*N*′)]

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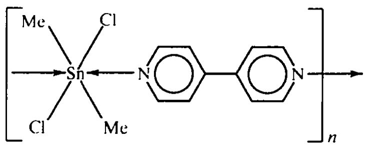
## Abstract

The 4,4′-bipyridine moiety in the title compound, $[SnCl_2(CH_3)_2(C_{10}H_8N_2)]_n$, bridges adjacent dichlorodimethyltin molecules to form a linear chain, whose six-coordinate Sn atom exists in an all-*trans* $O_h$ geometry.

## Comment

Dimethyltin dichloride (Davies *et al.*, 1970) forms a 2:1 complex with pyrazine, regardless of the stoichiometry of the reactants, when the reaction is carried out in an anhydrous solvent. The centrosymmetric $[(CH_3)_2SnCl_2]_2.C_4H_4N_2$ complex is five-coordinate, but the trigonal-bipyramidal geometry of the Sn atom is distorted towards an octahedron owing to a tin–chlorine bridge, which connects adjacent molecules into a linear chain. The crystal structure also features an unusually long Sn—N bond [*cf.* 2.746 (8) (Rivarola *et al.*, 1987) and 2.746 (6) Å (Cunningham *et al.*, 1988)]. Reactions of the Lewis acceptor with ligands having two basic nitrogen sites sometimes yield dimeric tetramethyldichlorodistannoxane; aminomethyl-2-pyridine catalyzes the hydrolysis of dimethyltin dichloride in moist solvents (Crowe *et al.*, 1979), as does pyrazine (Cunningham *et al.*, 1988). The Sn—N bond in the 2:1 complex is longer than that [2.62 (1) Å] in $[(CH_3)_2ClSn(CH_2)SnCl(CH_3)_2]_2.C_4H_4N_2$ (Austin *et al.*, 1987); the Lewis acidity of tin in this tetranuclear triorganotin complex is much reduced compared with that of dimethyltin chloride. Curiously, pyrazine furnishes an unambiguously six-coordinate 1:1 complex with dimethyltin dibromide in which the bond dimensions involving the Sn atom are normal (Rivarola *et al.*, 1987).

The 4,4′-bipyridine complex with dimethyltin dichloride, (I), which was synthesized in 95% ethanol, shows no evidence of decomposition when exposed to air. The Sn atom is six-coordinate in an all-*trans* octahedral geometry. The Sn—N bond distance [Sn—N 2.402 (2) Å] is similar to that [2.40 (1) Å] found in $[(CH_3)_2SnBr_2].C_4H_4N_2$ (Rivarola *et al.* 1987), but is somewhat longer than those found in the 1:2 complexes with monodentate imidazole [2.312 (2) Å; Martinez *et al.*, 1990] and *N*-methylimidazole [2.329 (5) Å; Bardi *et al.*, 1984], as well as those [2.29 (1) and 2.32 (1) Å] found in the chelated dimethyltin dibromide complex of *N*,*N*′-dimethyl-2,2′-biimidazole (Lopez *et al.*, 1992). The 4,4′-bipyridine moiety is flat, the two pyridyl rings being constrained by symmetry to be coplanar.



(I)

Although 4,4′-bipyridine has been extensively used in transition metal chemistry for the construction of chains, rectangular grids and cages (Tong, Cai *et al.*, 1998; Tong, Ye *et al.*, 1998), its use in main-group chemistry appears to be limited; the first structural account of a tin complex describes the isostructural 2:1 tri-*p*-tolyltin halide complexes in which the 4,4′-bi-